Accelerating Materials Discovery for Global Competitiveness Focus Topic
Room: 114 - Session MG+BI+MS+NS+TF-MoM

Development of Novel Materials
Moderator: Talat Rahman, University of Central Florida

9:00am **MG+BI+MS+NS+TF-MoM3 Molecular Engineering of Dyes for Dye-Sensitized Solar Cells via Rational Design**, ***Jacqueline Cole***, University of Cambridge, UK **INVITED**

Dye-sensitized solar cells (DSCs) have unique attributes that afford them prospective applications as smart windows - windows in buildings that generate electricity from sunlight. This electricity will be fed into a local grid that will create sustainable buildings for future cities.

Materials discovery of new DSC dyes is one of the remaining bottlenecks to technological progress of smart windows. This talk shows we are attempting to overcome this materials bottleneck via two complementary routes to molecular design: (i) a 'top down' approach that uses large-scale data mining to identify brand new classes of DSC dyes [1]; (ii) a 'bottom up' approach that computationally transforms well-known non-DSC dyes into suitable DSC dyes [2,3].

The 'top down' approach involves large-scale data-mining to search for appropriate dye candidates [1]. Here, structure-property relationships for DSC dyes have been codified in the form of molecular dye design rules, which have been judiciously sequenced in an algorithm to enable large-scale data mining of dye structures with optimal DSC performance. This affords, for the first time, a DSC-specific dye-discovery strategy that predicts new classes of dyes from surveying a representative set of chemical space. A lead material from these predictions is experimentally validated, showing DSC efficiency that is comparable to many well-known organic dyes.

The 'bottom up' approach concerns case studies on families of well-known laser dyes that are transformed into functional DSC dyes using molecular engineering [2,3]. The underlying conceptual idea is to implement certain electronic structure changes in laser dyes, using molecular engineering, to make DSC-active dyes; while maintaining key property attributes of the laser dyes that are equally attractive to DSC applications. This requires a concerted experimental and computational approach; results predict new dye co-sensitizers for DSC applications.

References

[1] J. M. Cole, K. S. Low, H. Ozoe, P. Stathi, C. Kitamura, H. Kurata, P. Rudolf, T. Kawase, "Data Mining with Molecular Design Rules Identifies New Class of Dyes for Dye-Sensitised Solar Cells" *Phys. Chem. Chem. Phys.* 48 (2014) 26684-90

[2] S. L. Bayliss, J. M. Cole, P. G. Waddell, S. McKechnie, X. Liu, "Predicting solar-cell dyes for co-sensitization", *J. Phys. Chem. C* 118 (2014) 14082–14090

[3] F. A. Y. N. Schroeder, J. M. Cole, P. G. Waddell, S. McKechnie, "Transforming benzophenoxazine laser dyes into chromophores for dye-sensitized solar cells: a molecular engineering approach", *Advanced Energy Materials* (2015) DOI: 10.1002/aenm.201401728

10:40am **MG+BI+MS+NS+TF-MoM8 Controlled Spontaneous Nanoscale Patterning of Nonstoichiometric Reconstructions for Catalysis and Light Harvesting**, *J.M. Martirez, D. Saldana-Greco*, University of Pennsylvania, *W.A. Saidi*, University of Pittsburgh, *J.S. Lim*, ***Andrew Rappe***, University of Pennsylvania **INVITED**

The ability to manipulate the atomic and electronic structure and stoichiometry of surfaces is of utmost importance in optimizing heterogeneous catalysts. A critical requirement in this endeavor is a deep thermodynamic and kinetic understanding of surface reconstruction behavior, under various thermal and chemical constraints. We explore the reconstruction behaviors of Ti- and Mn-based perovskite type oxides: $BaTiO_3$, $PbTiO_3$, and $CaMnO_3$: the former two exhibit ferroelectricity, while the latter undergoes surface-induced magnetic ordering. Due to the characteristic properties of these oxides, we investigate the effect of their switchable polarization (for ferroelectric oxides) and near surface magnetic ordering ($CaMnO_3$) in their surface phase evolution, in addition to the effects of temperature and the chemical potentials of their constituent elements. We find that these oxides undergo surface reconstruction transformations that generally result in enrichment of their catalytically active components (Ti and Mn). These reconstructions show rich bonding and structural motifs that affect the active sites' reactivity and accessibility. Furthermore, these surface transformations, as in $BaTiO_3$ and $PbTiO_3$, can be tuned with the help of an electric field. An applied electric field changes the material's polarization, which then alters the surface electronic properties, and thereby also affects their sensitivity towards stoichiometric changes. In addition to the thermodynamic understanding of the surface reconstructions, we introduce the kinetic tunability of the surface reconstruction. We demonstrate this from a particular surface phase coexistence observed in $BaTiO_3$, namely the *c*(2x2) and *c*(4x4), where the diffusion behavior of the TiO units that compose both surfaces strongly dictate their degree of agglomeration. Finally, based on our interest in $CaMnO_3$ (001) surfaces, we have started to explore the more complex $CaMn_7O_{12}$. The electronic properties of this oxide yield interesting physical phenomena including charge ordering, non-collinear magnetism and improper ferroelectricity. We are currently investigating the ground state non-collinear magnetic configuration in this compound and its role on the stability of the charge-ordered state.

11:20am **MG+BI+MS+NS+TF-MoM10 Developing Evolutionary Algorithms for *a priori* Crystal Structure Prediction and Applications towards Novel Pressure-Stabilized Materials**, ***Eva Zurek***, University at Buffalo-SUNY **INVITED**

One way to accelerate the development of new materials is via *a priori* crystal structure prediction (CSP) of hitherto unknown systems, followed by the computation of their properties and determination of promising synthesis conditions. A number of algorithms designed to solve global optimization problems have recently been applied to CSP with much success, and evolutionary algorithms (EAs) have emerged as one of the most promising methods for systems where little or no experimental data is available. Therefore, we have developed the open-source XtalOpt EA for CSP as an extension to the widely used chemical builder and visualizer, Avogadro. In this talk we present new developments within XtalOpt that allow it to successfully predict the structures of crystals with larger and more complex unit cells. Furthermore, we summarize the application of XtalOpt towards the prediction of hydrogen-rich solids with unique stoichiometries that are computed to be stable at pressures that are attainable within diamond anvil cells. The influence of the structure of the hydrogenic lattice on the electronic structure and the propensity for high temperature superconductivity is discussed.

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